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NONENZYMATIC BROWNING IN MODEL SYSTEMS CONTAINING SUCROSE

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FOREWORD

This report was prepared at the Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Mass., under task No. 775803 and contract No. AF41(609)-2981. Major Norman D. Heidelbaugh and Major William T. Ashby, of the Physiology Branch of the USAF School of Aerospace Medicine, monitored the project.

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This report has been reviewed and is approved.

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ABSTRACT

Freeze-dried systems containing sucrose and organic acids were found to undergo rapid nonenzymatic browning, even at low relative humidities. Addition of protein reduced the rate of browning, especially at low humidities. It was determined that the browning was due to reducing sugars produced by acid-catalyzed hydrolysis of sucrose. This hydrolysis occurred even when water content was well below 1% and below B.E.T. monolayer coverage (Brunauer-Emmett-Teller method of calculating monolayer values).

These findings have important implications for storage stability of dehydrated foods since they point to a new mechanism for initiation of browning in such foods as freeze-dried juices.

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I. INTRODUCTION

During our study of deteriorative reactions in freeze-dried model systems at 55° C., experiments were performed on the browning of model systems containing carbohydrates, lipids, and proteins. It is well known that many foods of similar composition brown at high temperatures and high humidities. The reaction is usually attributed to interaction between reducing sugars and free amino groups of the protein (1). Our results indicate, however, that hydrolysis of sucrose may occur when water content is relatively low, and that the reducing sugars formed participate in browning.

II. EXPERIMENTAL PROCEDURES

Sample preparation

As shown in table I, model systems were prepared by mixing the components in an Omni-Mixer, with subsequent freeze-drying of

TABLE I

Composition of model systems (runs 1 and 2)

Component	Weight of component (gm.)				
	Run 1		Run 2		
	Model A	Model B	Model C	Model D	Model E
Carbohydrates					
Glucose	—	66.8	—	—	—
Sucrose	133.6	66.8	150	150	150
Malic acid	4.0	4.0	—	—	—
Citric acid	—	—	—	5.0	5.0
Avicel	9.6	9.6	10	10	10
Egg albumin	2.8	2.8	—	—	5
Methyl oleate	3.8	3.8	—	—	—
Water	46.0	46.0	40	40	40
Moisture content (grams of water per 100 gm. of solids) at:					
0.1% RH	<0.31	5.42	0.11	0.22	0.39
31% RH	0.50	7.39	0.33	0.47	3.85
50% RH	0.98	10.24	—	—	—
75% RH	—	—	0.95	3.72	5.67

samples (4 to 5 gm.) according to the methods of Maloney et al. (2). After being dried, the samples were humidified to the desired relative humidities over saturated salt solutions and then stored at 55° C.

Browning pigments

The procedure of Choi et al. (3) was modified as follows: Samples of dry material (2 to 5 gm.) were dispersed in 20 ml. water, and 2.5 ml. of 10% fresh trypsin suspension were added. After one-hour incubation at 45° C., 2 ml. of 50% trichloroacetic acid and 0.1 gm. of filter aid were added. After mixing and filtration, the optical density at 400 mμ was measured on the clear solution, with the enzyme blank set at 100% transmission. The results are reported as optical density per gram sample multiplied by 100.

Reducing sugars

Samples of dry material (2 to 5 gm.) were extracted with 25 ml. water for one-half hour and then filtered. A modified Somogyi reducing sugar test (oxidation of copper to Cu_2O) was performed on 5 ml. of the filtrate (4).

III. RESULTS AND DISCUSSION

Two model systems were studied in run 1. Their composition is shown in table I, and the extent of browning at three different relative humidities is shown as a function of time in figure 1. As expected, substantial browning

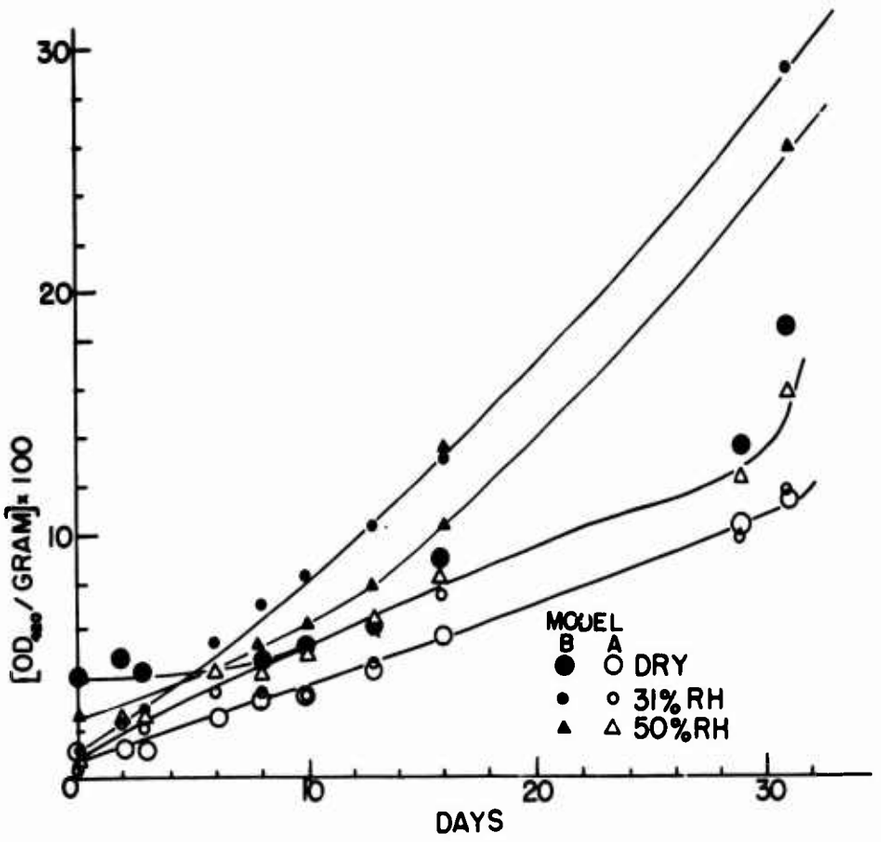

FIGURE 1

Nonenzymatic browning, run 1 (55° C.).

occurred in the system containing glucose. However, the system containing sucrose as the only added carbohydrate also browned considerably, even at very low water contents.

The possibility that the browning was due to carbonyl compounds produced during autoxidation of the lipid was considered, but sensitive thin-layer chromatographic tests for peroxide content showed that oxidation level of the methyl oleate was negligible. Therefore, the possibility that sucrose was being hydrolyzed was considered, and a further study was undertaken in run 2.

In run 2, three model systems (C, D, and E) were studied. Their composition is given in table I: lipid and glucose were eliminated; and citric acid, instead of malic acid, was used because of its higher solubility. However, one of the systems was prepared without any protein or citric acid (model C), and one without protein but with citric acid (model D).

The extent of browning for the three models, each held at three water activities, is shown in figure 2. Obviously, when acid is lacking, the model system (model C) is stable and does not brown. In the presence of acid, but without protein (model D), significant browning occurs even at extremely low humidities (moisture content at 0.22 gm. of H_2O per 100 gm. of solids). Protein added to one system (model E) seemed to act as a buffer, possibly by reducing the concentration of hydrogen ions in the surface water.

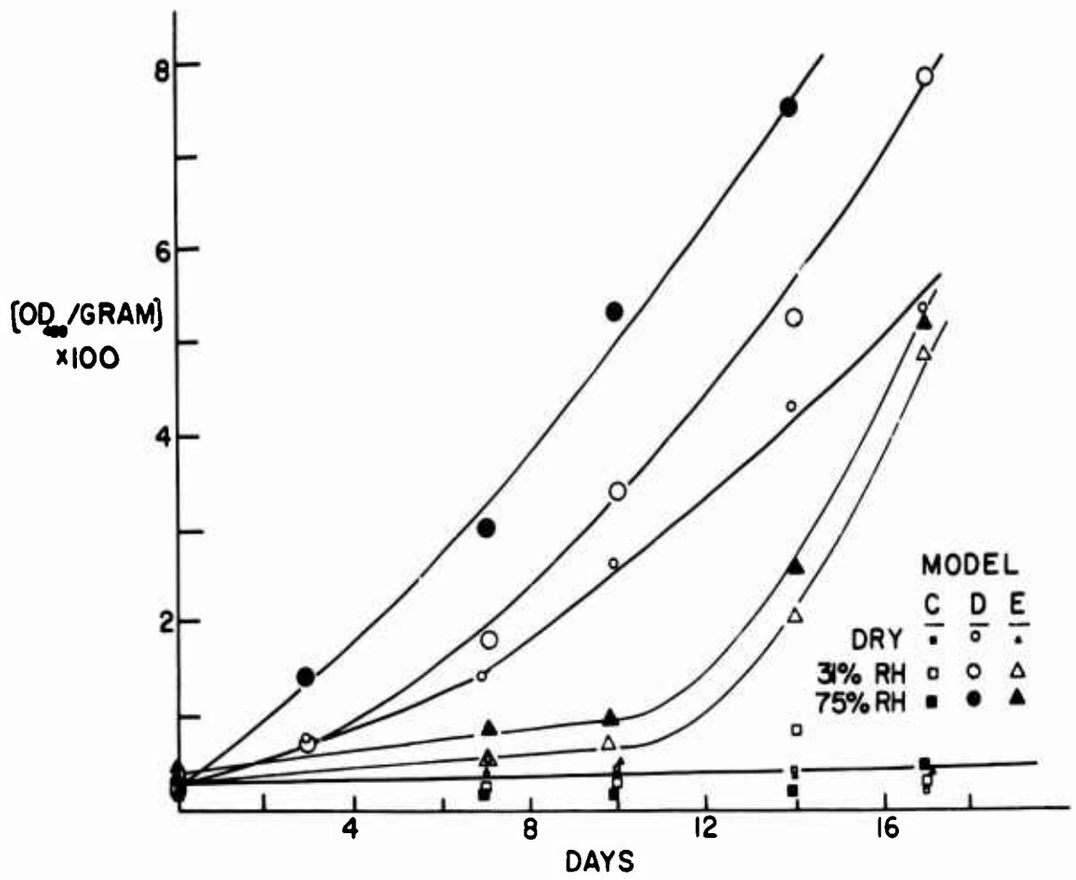

FIGURE 2

Nonenzymatic browning, run 2 (55° C.).

These results support the hypothesis that hydrolysis of sucrose can occur in freeze-dried systems and produce reducing sugars which then participate in browning reaction. The hypothesis was confirmed further by direct determination of reducing groups. The results are presented in table II. As browning becomes significant, products of this reaction also give a positive reducing sugar test. This fact may be responsible for the variability of results obtained at high moisture contents.

The study shows that in model systems containing sucrose and citric acid, at low moisture content, hydrolysis of sucrose can occur and lead to nonenzymatic browning. The mechanism of this reaction requires the participation of water as well as the dissolution of sucrose in the aqueous phase (5). The results presented here indicate that the reaction not only can occur even at very low water contents but, in fact, occurs below the monolayer coverage as estimated from water sorption isotherms of these systems (6).

TABLE II

Hydrolysis (in percentage) of sucrose (run 2)

Time (days)	Model C			Model D			Model E		
	Dry	31% RH	75% RH	Dry	31% RH	75% RH	Dry	31% RH	75% RH
0	0.15	0.05	0.06	1.45	1.81	8.05	0.91	0.96	2.43
3	0.09	0.03	0.09	2.83	6.62	41.3	1.13	4.79	11.96
7	0.13	0.06	0.09	5.26	8.14	70.4	0.85	15.87	21.68
10	0.12	0.05	0.11	5.22	6.51	69.6	2.91	14.42	16.20
14	0.13	0.07	0.12	7.89	10.97	73.8	2.81	15.58	25.80
17							2.81	18.06	40.37
22							3.25	16.54	36.05

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